A NOTE ON THE ELECTROSTATIC MODEL OF HYDROGEN BOND APPLIED TO HYDROGEN BONDING IN ANILINE AND SUBSTITUTED ANILINES IN DIFFERENT ENVIRONMENTS

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ABSTRACT Coggeshall's method of treatment of the electrostatic model of hydrogen bond has been applied to the case of hydrogen bonding in solutions between the molecules of aniline or of substituted anilines and the molecules of some polar solvents and also to the case when such bonds are formed between similar molecules in the liquid state of the pure compounds. It is pointed out that in the case of such a model, the ratio of the values of the sum of the solvent shifts in the frequencies of N-H stretching vibrations of a particular compound in solutions in two different solvents should be independent of the nature of the compounds. In the case of the pure liquids, on the other hand, the ratio of the sum of the frequency shifts to the geometric mean of the frequencies of symmetric and asymmetric N-H stretching vibrations for the different compounds is expected to remain constant. The data reported previously are found to conform to these expectations. Moreover, the experimental fact that the ratio of the sum of the solvent shifts in the frequencies of the two N-H stretching vibrations of a particular compound in a certain solvent to that of aniline in the same solvent is a constant for the compound and is approximately independent of the nature of the solvent, has been satisfactorily accounted for on the basis of the model.

INTRODUCTION

Since Pauling (1928) proposed that the hydrogen bond is electrostatic in nature, many authors (Sack and Prigogine, 1941, Maladière and Magat, 1947; Maladière 1948, Coggeshall, 1950; Shigorin and Dokunikhin, 1955) have calculated the spectroscopic properties of hydrogen bonds using such models. Coggeshall (1950) theoretically investigated the frequency shift, the intensity of absorption and the energy of association of a hydroxyl group which is participant in a hydrogen bonded complex by solving the Schrodinger equation for a hydroxyl group treated as a diatomic molecule with a Morse potential energy function to which the polarisation energy of a hydroxyl group due to electrostatic interaction has been added. He found that the stretching vibrational frequency of the hydrogen-bonded O-H group in benzyl alcohol and catechol calculated by the above method agrees well with the experimentally observed values. Coggeshall also showed that,

for small vibrations, considerations based on partial ionic and covalent characteristics of the hydroxyl group also yield frequencies in fair agreement with experiment. Venkata Ramiah and Puranik (1962a, b) applied the latter method with some modifications to the calculation of the stretching vibrational frequencies of hydrogen bonded N-H bonds in amides and of O-H bonds in acids and alcohols and achieved fair agreement with the observed values. In all these cases the frequency change due to hydrogen bonds formed between similar molecules have been calculated, but no such calculations based on the electrostatic model of hydrogen bonds formed between two dissimilar molecules viz., a solvent and a solute molecule have been made. Medhi and Kastha (1963a, b) have studied hydrogen bonding in aniline and substituted anilines in the liquid state and in solutions in some polar solvents. They have observed that the ratio of the sum of the solvent shifts in the frequencies of symmetric and asymmetric N-H stretching vibrations of a particular aniline compound in a certain solvent to that of aniline in the same solvent is a constant which is almost independent of the nature of the solvent. Moreover, the value of the constant was found to be greater than unity for compounds whose molecules contain electronegative atom or group of atoms (for which Hammett σ factor is positive), while for compounds with molecules containing a electropositive group (Hammett σ factor negative) the value of the ratio is less than unity. It is the purpose of the present paper to find out how far the electrostatic model of hydrogen bonds treated by Coggeshall can explain some of the observed facts qualitatively.

COGGESHALL MODEL APPLIED TO N-H..X BOND

In applying the model of Coggeshall to hydrogen bonds formed between the H-atom in one of the N-H bonds of the molecule of aniline or any substituted aniline and an atom X (where X = O or N) in the molecule of the solvent the following simplifying assumptions have been made.

(1) The solutions are so dilute that only the interaction between a single molecule of the solute and a molecule of the solvent need be considered.

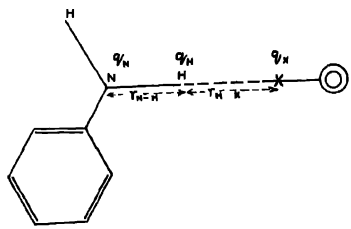

Fig 1.

Linear hydrogen bond N—H.. X between a molecule of Phenyl amine and a molecule of a Polar solvent.

(ii) The hydrogen bonds N-H...X are always very nearly linear. (*cf.* Pimentel and McClellan, 1960) as shown in Fig. 1.

(iii) The distance $r_{H\text{-}X}$ is almost the same in the case of solution of aniline and of substituted anilines in the polar solvent whose molecule contains the atom X.

(iv) The bond length $r_{N\text{-}H}$ in the molecules of the various phenyl amines is approximately constant

It is assumed that all these considerations apply to those aniline compounds where the substituent is neither very electronegative nor offers steric hindrances. In the following paragraphs the physical quantities associated with a substituted aniline compound with a definite Hammett σ-factor are designated with a superscript σ.

(a) *X representing an atom of nitrogen or of oxygen in the molecule of the solvent*

The force constant for the stretching of N-H bond in the various phenyl amines is calculated from the equation $f^\sigma = 2.76 \times 10^{-2}\ (\nu_a^{\sigma 2} + \nu_s^{\sigma 2})$ dynes/cm and is related to the dissociation energy D_0 in K. Cal/mole of the normal covalent N-H bond through the relation $f^\sigma = 2a^{\sigma 2}D_0$, where a^σ is a constant, which is slightly different for different molecules in the series of phenyl amines investigated, in the expression of the vibrational potential function of the Morse type used by Coggeshall (1950). Remembering that $\nu_a^\sigma = \nu_s^\sigma(1+\delta)$, where δ is small, we find the total solvent shift $\Delta\nu_t^\sigma$ $(= \Delta\nu_a^\sigma + \Delta\nu_s^\sigma)$ is given by $\Delta\nu_t^\sigma = 6.02\, a^\sigma D_o^{-1/2}.\Delta D^\sigma$ .. (1), where $\Delta D^\sigma = D_0 - D^\sigma$, D^σ being the dissociation energy in K Cal/mole of the hydrogen bonded N-H bond According to Coggeshall (1950) $D^\sigma = D_0 - (F_1/F_2)^\sigma\beta$, where D_0 is the dissociation energy in K Cal/mole of a normal covalent N-H bond and β, also in K. Cal/mole, is the energy due to ionic character of the N-H bond $(F_1/F_2)^\sigma$ represents the ratio of the electrostatic forces exerted by the unbalanced charges q_X on X and q_N on N respectively on the unbalanced charge q_H on H and is given by,

$$(F_1/F_2)^\sigma = \frac{q_X}{r^2_{H\cdots X}} \Big/ \frac{q_N}{r^2_{N\text{-}H}} \qquad \ldots\ (2)$$

It is seen from eqn. (1) that for the same compound dissolved in two different polar solvents whose molecules contain the atoms X_1 and X_2 respectively, the ratio of the total solvent shift in the two solvents is given by, $(\Delta\nu_t^\sigma)_1/(\Delta\nu_t^\sigma)_2 = \dfrac{D_0 - D_1^\sigma}{D_0 - D_2^\sigma}$

Substituting the values of D_1^σ and D_2^σ and using equation (2) we obtain,

$$(\Delta\nu_t^\sigma)_1/(\Delta\nu_t^\sigma)_2 = (F_1/F_2)_1^\sigma/(F_1/F_2)_2^\sigma = \frac{q_{X_1}}{q_{X_2}} \cdot \frac{r^2_{H\text{-}X_2}}{r^2_{H\text{-}X_1}} \qquad \ldots\ (3)$$

Eqn. (3) shows that the value of the above ratio for the different compounds

dissolved in the same pair of solvents is a constant for the particular pair of solvents and is independent of the nature of the compounds. The value of the ratio computed from the total solvent shifts for a number of aniline and substituted anilines in solutions in acetone, ether, tetrahydrofuran and pyridine as obtained by Medhi and Kastha (1963b) are given in Table 1. The approximate constancy of the ratio for a pair of solvent is evident.

Now, if we compare the value of the total solvent shift ($\Delta\nu_t^{\sigma}$) for a substituted aniline compound with that of aniline ($\Delta\nu_t^{0}$), both in solution in the same solvent, we find from eqn. (1)

$$\Delta\nu_t^{\sigma}/\Delta\nu_t^{0} = \frac{a^{\sigma}}{a^{0}} \cdot \frac{D_0 - D^{\sigma}}{D_0 - D^{0}}$$

TABLE I

Compound	$\frac{(\Delta\nu_t^{\sigma})\ \text{Pyridine}}{(\Delta\nu_t^{\sigma})\ \text{Acetone}}$	$\frac{(\Delta\nu_t^{\sigma})\ \text{Tetrahydrofuran}}{(\Delta\nu_t^{\sigma})\ \text{Acetone}}$	$\frac{(\Delta\nu_t^{\sigma})\ \text{Ether}}{(\Delta\nu_t^{\sigma})\ \text{Acetone}}$
Aniline	2.25	1.58	1.12
m-Phenetidine	2.16	1.54	1 16
m-Anisidine	2 12	1 50	1.06
p-Anisidine	2 20	1 40	1.22
m-Toluidine	2.22	2 10	1.25
o-Nitroaniline	2.10	1.53	1.18

Substitution of the values of D^{σ} and D^{0} and use of eqn. (2) yield

$$\frac{\Delta\nu_t^{\sigma}}{\Delta\nu_t^{0}} = \frac{a^{\sigma}}{a^{0}} \cdot (F_1/F_2)^{\sigma}/(F_1/F_2)^{0} = \frac{a^{\sigma}}{a_0} \cdot \frac{q_N^{0}}{q_N^{\sigma}} \cdot \left(\frac{r^{\sigma}_{N-H}}{r^{0}_{N-H}}\right)^2$$

If we assume $a^{\sigma} \approx a^{0}$ and $r^{\sigma}_{N-H} \approx r^{0}_{N-H}$ then the value of the above ratio, denoted by S^{σ} becomes,

$$S^{\sigma} = \frac{\Delta\nu_t^{\sigma}}{\Delta\nu_t^{0}} \approx \frac{q_N^{0}}{q_N^{\sigma}}$$

It is seen from the relation that the value of S^{σ} is a constant for a particular compound and is independent of the nature of the solvent as has been observed by Medhi and Kastha (1963b). The charge $q^{\sigma}{}_N$ on the N-atom in the molecule of a substituted aniline compound consists of two parts, a negative unbalanced charge $-Q^{\sigma}$ originating from the bond moments of the various localised bonds in the molecule and a part $+q_{\pi}{}^{\sigma}$ arising from the migration of charge from the N-atom into the delocalised π-orbitals of the molecule. If the values of the first portion

of the unbalanced charge for the various substituted anilines are not much different from that for aniline, then $S^\sigma = \frac{-Q^\sigma + q_\pi{}^0}{-Q^\sigma + q_\pi{}^\sigma} \approx \frac{-Q + q_\pi{}^0}{-Q + q_\pi{}^\sigma}$. The charge $q^\sigma{}_\pi$ will in general be greater or smaller than $q_\pi{}^0$ depending on whether the substituent in the given position in the molecule of the particular compound is electronegative or electropositive respectively in comparison to the H-atom in the same position of the aniline molecule.

Thus for the electronegative groups Cl and NO_2 the value of S^σ is greater than unity, while in the case of the electropositive methyl group the value of S^σ is less than unity. Since the Hammett σ factor for the electronegative atom or group of atoms is positive and that for electropositive group is negative, the foregoing discussion explains the observed facts mentioned in the introduction.

(b) *X-representing the N-atom in the NH_2 group in the molecule of the phenyl amines.*

In the case of aniline and some substituted aniline compounds in the liquid state the hydrogen bonding takes place between the H atom of the NH_2 group of one molecule and the N-atom in the NH_2 group of another molecule as shown in Fig. 2.

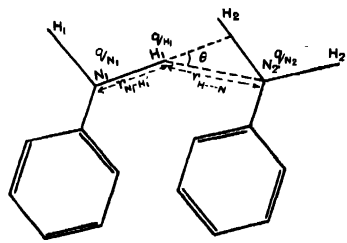

Fig. 2.
Bent hydrogen bond N—H...N between two molecules of aniline in the liquid state.

The N-H...N bridge in the figure is pictured as slightly bent, however, for $\theta = 0$, the linkage becomes linear.

The relation in eqn. (1) can be written in the slightly different form .

$$\Delta\nu_t{}^\sigma = (\nu_a{}^\sigma \nu_s{}^\sigma)^{\frac{1}{2}} \Delta D^\sigma / D_0 \qquad (4)$$

Substituting the value of ΔD^σ in eqn. (4) and replacing F_1 by $F_1 \cos\theta$, the component along N_1H_1 of the electrostatic force exerted by the charge q_{N2} on the N-atom of second molecule on the charge q_{H1} on the H-atom of the first molecule, we obtain

$$(\nu_a{}^\sigma \nu_s{}^\sigma)^{-\frac{1}{2}} \Delta\nu_t{}^\sigma = \frac{\beta}{D_0}\left(\frac{F_1 \cos\theta}{F_2}\right)^\sigma = \left(\frac{r^\sigma{}_{N\text{-}H}}{r_{H\ldots N}}\right)^2 \cdot \frac{\beta}{D_0}\cos\theta \qquad \ldots \quad (5)$$

If the values of θ, $r^{\circ}_{N\text{-}H}$ and $r_{H\ldots N}$ are not much different for the various phenyl amines then the values of $(\nu_a^{\circ}\nu_s^{\circ})^{-\frac{1}{2}}\Delta\nu_t^{\circ}$ are expected to be almost the same in all the compounds The values of the quantity computed from the data on $\Delta\nu_t^{\circ}$, ν_a° and ν_s° obtained by Medhi and Kastha (1963b) for aniline and some substituted aniline compounds are given in Table II. The value is seen to be approximately the same for the different compounds.

TABLE II

Compound	$(\nu_a^{\circ}\nu_s^{\circ})^{-\frac{1}{2}}\Delta\nu_t^{\circ}$
Aniline	029
m-Chloroaniline	.024
m-Anisidine	.022
p-Anisidine	.024
m-Phenetidine	.023
m-Toluidine	.023
p-Toluidine	.022

From the above discussions it is seen that the electrostatic model of hydrogen bonds treated by Coggeshall fairly explains the observed facts qualitatively.

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